70

ELECTRONIC ENERGY-STATES OF ONE-DIMENSIONAL MIXED CRYSTALS

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ABSTRACT. The electronic energy-states of mixed linear lattices have been investigated by a matrix method which is the same as used by the author in a previous paper (Referred to as I in the text) for studying the electronic energy states of linear monoatomic lattices. As in I, the models in this paper have been constructed in the frame-work of rectangular potential well. Explicit equations for allowed electronic energies have been given for several perfect and disordered cases. The results for the disordered cases have been given only upto first order. Some of the results are in a form suitable for numerical computations.

INTRODUCTION

By using a matrix method, the author (Roy 1966) has investigated in an earlier paper (Referred to as paper I henceforward) the electronic energy states in one dimensional monoatomic crystals. In this paper, the same method has been used to study the electronic energy-states in one dimensional mixed crystals.

James and Ginzbarg (1953) and Landauer and Helland (1954) have studied in a practical way the electronic energy-states of mixed linear lattices in which groups of different species of atoms are connected in a chain with varying degrees of complexity. A theorem of Saxon and Hunter (1949) answers to some extent the question as to what properties of a mixed lattice can be inferred from a knowledge of the separate band-structure of the pure lattices. This theorem states that the common forbidden energies of two pure δ-function lattices θ and ϕ remain forbidden in any mixture of θ and ϕ. A proof of this theorem in a somewhat general way has been given by Luttinger (1954). However, limitations have been pointed out about the validity of the theorem as well as its proof. James and Ginzbarg (1953) have analysed the theorem by applying the method of mode counting while Kerner (1954) has used a matrix method. These investigations have brought out that the theorem of Sanon and Hunter is true only for δ-potentials. Kerner's analysis has broadened the condition for the persistence of the forbiddenness of any energy simultaneously forbidden in pure θ and ϕ crystal. The knowledge of the electronic energy-bands of the θ and ϕ crystals can thus supply information only on a limited scale about the electronic energy-states of the mixed θ—ϕ crystal. The best way to get such information would be to know the equations giving the allowed electronic energies for the particular type of mixing under consideration.

In this paper, investigations have been made about the electronic energy-states in some one-dimensional mixed crystals within the frame work of the rectangular potential-well model. Explicit energy-eigenvalue equations have been derived for various ordered and disordered models. Some of these equations are in a form suitable for numerical computations. A matrix method has been used for investigation of the problems of this paper. This method, as mentioned before, is the same as used in I where a thorough discussion has been given about the importance of rectangular potential well model compared to the δ-function model.

EIGENVALUE EQUATIONS FOR PERFECT INFINITE LATTICES

Mixed lattice of general type. we consider the derivation of the energy eigenvalue equation for a mixed lattice as shown in the Fig. 1 below :

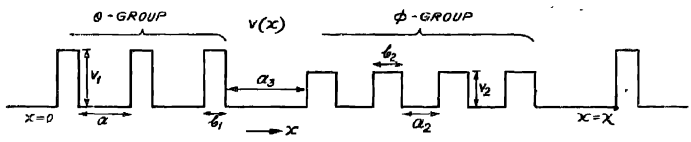

Fig. 1

Rectangular potential-well model for a one-dimensional infinite mixed lattice of a general type.

The model is formulated with an infinite 'no of' two types of atoms θ and ϕ producing potentials of rectangular well type. The parameters with suffix 1 refer to the θ-atoms while those with suffix 2 refer to the ϕ-atoms. In the model, we suppose that the sequence with l no of θ atoms followed by m no of ϕ-atoms is repeated infinitely. The distances a_1, a_2, a_3, separating respectively two θ-atoms, two ϕ-atoms and the groups of θ and ϕ atoms are all different. This makes the model somewhat general. The period χ of the lattice is obviously given by :

$$\chi = (l-1)a_1+(m-1)\ a_2+lb_1+mb_2+2a_3 \qquad \ldots \quad (1)$$

Referring to equation (34) of I, we find that the eigenvalues for the present model are given by :

$$\cos \mu\chi = \tfrac{1}{2} \operatorname{tr} T \qquad \ldots \quad (2)$$

T is defined through the equation :

$$\begin{pmatrix} A \\ B \end{pmatrix}_{at\ x\,=\,\chi} = T \begin{pmatrix} A \\ B \end{pmatrix}_{at\ x\,=\,0} \qquad (3)$$

A and B have meanings as in equation (4) of I. As explained in I, T can be written as a product of some other matrices in the following form :

$$T = \begin{pmatrix} \exp i\alpha(a_3-a_2) & 0 \\ 0 & \exp -i\alpha(a_3-a_2) \end{pmatrix} (T_\varphi)^m \begin{pmatrix} \exp i\alpha(a_3-a_1) & 0 \\ 0 & \exp -i\alpha(a_3-a_1) \end{pmatrix} (T_\theta)^l \quad \ldots (4)$$

In equation (4), T_θ and T_φ are the same as T-matrix of I with appropriate parameters for θ and ϕ type atoms. Thus following equations (19) to (22) of I, we find the following expressions for the elements of the T_θ -matrix :

$$(T_\theta)_{11} = \frac{1}{4i\alpha\beta_1} \cdot [(i\alpha+\beta_1)^2 \exp(\beta_1 b_1 + i\alpha a_1) - (i\alpha-\beta_1)^2 \exp(-\beta_1 b_1 + i\alpha a_1)] \quad \ldots (5)$$

$$(T_\theta)_{22} = (T_\theta)_{11}^* \quad (6)$$

$$(T_\theta)_{21} = \frac{1}{4i\alpha\beta_1} [(i\alpha+\beta_1)(i\alpha-\beta_1) \exp(-i\alpha a_1)\{\exp(\beta_1 b_1) - \exp(-\beta_1 b_1)\}] \quad (7)$$

$$(T_\theta)_{12} = (T_\theta)_{21}^*$$

The elements of T_φ-matrix are given by expressions exactly similar to those of (5) to (8) with suffix 1 replaced by suffix 2. Since $\det T_\theta = \det T_\varphi = 1$, we notice from (4) that $\det T = 1$. Now if $\frac{1}{2}\,\mathrm{tr}\, T_\theta = \cos c_\theta$, the eigen values of T_θ are $\exp(\pm ic_\theta)$. Following equations (50) and (51) of I, we then find the following expressions for the elements of $(T_\theta)^l$:

$$(T_\theta{}^l)_{11} = (T_\theta{}^l)_{22}{}^* = \frac{1}{\sin c_\theta} \{\sin(l+1)c_\theta - (T_\theta)_{11}{}^* \sin c_\theta\} \quad \ldots (9)$$

$$(T_\theta{}^l)_{21} = (T_\theta{}^l)_{12}{}^* = (T_\theta)_{21} \frac{\sin lc_\theta}{\sin c_\theta} \quad \ldots (10)$$

Exactly similar expressions are obtained for the elements of $(T_\varphi)^m$ by replacing l by m and the suffix θ by ϕ. With proper expressions for the elements of $(T_\theta)^l$ and $(T_\varphi)^m$, we get from equations (2) and (4), the following equation for the electronic energy-eigenvalues :

$$\begin{aligned} \cos \mu\chi = {} & (I_\theta I_\varphi - J_\theta J_\varphi) \cos \alpha(2a_3 - 2a_2 - a_1) - (J_\theta I_\varphi + J_\varphi I_\theta) \cdot \\ & \sin \alpha(2a_3 - a_2 - a_1) + (\eta_\theta \eta_\varphi + \zeta_\theta \zeta_\varphi) \cdot \cos \alpha(a_1 - a_2) \\ & - (\zeta_\theta \eta_\varphi - \zeta_\varphi \eta_\theta) \sin \alpha(a_1 - a_2) \end{aligned} \quad \ldots (11)$$

where,

$$(T_\theta{}^l)_{11} = I_\theta + iJ_\theta \quad \ldots (12)$$

$$(T_\theta{}^l)_{21} = \eta_\theta + i\zeta_\theta \quad \ldots (13)$$

$$I_\theta = \frac{1}{\sin c_\theta}\{\sin (l+1)c_\theta - (T_\theta)_{11r} \sin lc_\theta\} \quad \ldots (14)$$

$$J_\theta = (T_\theta)_{11I} \frac{\sin lc_\theta}{\sin c_\theta} \quad \ldots (15)$$

$$(T_\theta)_{11} = (T_\theta)_{11r} + i(T_\theta)_{11I} \quad \ldots (16)$$

$$(T_\theta)_{21} = (T_\theta)_{21r} + i(T_\theta)_{21I} \quad \ldots (17)$$

The quantities I_φ, J_φ . . etc. are given by similar expressions with c_θ replaced by c_φ and l by m.

Special cases : We can now get some results as special cases of equation (11).

Case I : Let us consider the model as given by Fig. (2) below :

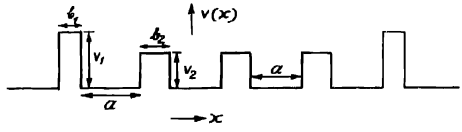

Fig. 2

Rectangular potential-well model of a special type of infinite mixed lattice (Kerner's model).

Here the atoms of one kind say the θ-type occur in groups of one and the group to group distances are the same as the interatomic distances of the other group. Thus in this case $l = 1$, $a_2 = a_1 = a_3 = a$(say). From (11), we get for the present case :

$$\cos \mu\chi = \frac{1}{\sin c_\varphi}\left\{\sin (m+1)c_\varphi \cos c_\theta - \sin mc_\varphi\left[\cos \hbar\beta_1 b_1 \cos \hbar\beta_2 b_2 - \frac{\beta_1^2+\beta_2^2}{2\beta_1\beta_2} \sin \hbar\beta_1 b_1 \sin \hbar\beta_2 b_2\right]\right\} \quad \ldots (18)$$

Equation (18) is the same as derived by Kerner (1954), starting with the model of Fig. 2.

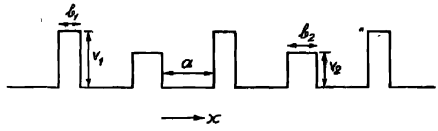

Fig. 3

Rectangular potential-well mode. for a one-dimensional infinite perfect diatomic lattice.

Case II : We now consider the model given by Fig 3 below · This is a model for an ideal diatomic crystal in the framework of rectangular potential-well.

Obviously for this model, $a_2 = a_3 = a_1 = a$ (say) and $l = m = 1$. Thus for this case, we get from (18) :

$$\cos \mu(2a+b_1+b_2) = \frac{(\beta_1^2+\alpha^2)(\beta_2^2+\alpha^2)}{4\alpha^2\beta_1\beta_2} \cdot \sin h\,\beta_1 b_1 \sin h\,\beta_2 b_2$$

$$- \frac{1}{4\alpha^2\beta_1\beta_2}(\beta_1^2-\alpha^2)(\beta_2^2-\alpha^2) \sin h\beta_1 b_1 \sin h\beta_2 b_2 \cos 2\alpha a$$

$$+ \frac{1}{2\alpha\beta_1\beta_2} \cdot [\beta_2(\beta_1^2-\alpha^2) \cosh \beta_2 b_2 \sinh \beta_2 b_2 + \beta_1(\beta_2^2-\alpha^2)\cosh \beta_1 b_1 \cdot$$
$$\cdot \sinh \beta_2 b_2] \sin 2\alpha a + \cosh \beta_1 b_1 \cosh \beta_2 b_2 \cos 2\alpha a \qquad \ldots (19)$$

Under the conditions $b_1 \to 0$, $b_2 \to 0$, so that $b_1 v_1$ and $b_2 v_2$ remain finite (δ-potentials for both θ and ϕ atoms), equation (19) reduces to the form given by the present author (Roy 1964) as well as Saxon and Hutner (1949)

EIGENVALUE EQUATIONS FOR DISORDERED MIXED LATTICES

Case I : Let us consider the model given by Fig. (4) below. The model contains 'n' no of θ-atoms and 'n' no of ϕ-atoms. The distances between any two potential wells are arbitrary. We suppose that $a_{j,j} = a + c_{j,j}$ = distance between the j-th θ-atom and j-th ϕ-atom, $a_{j,j+1} = a + \epsilon_{j,j+1}$ = distance

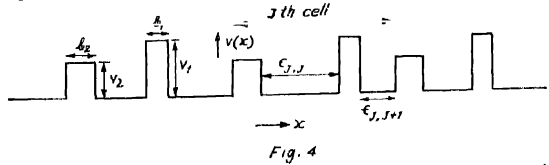

Fig. 4

Rectangular potential-well model for a one-dimensional finite diatomic lattice with a general type of disorder.

between j-th θ-atom and $(j+1)$th ϕ-atom. 'a' is the average of all $a_{j,j}$'s. Following equation (4), we find that the T-matrix T_j for the j-th cell in the present case is given by :

$$T_j = \begin{pmatrix} \exp i\alpha(a+\epsilon_{j,j+1} & 0 \\ 0 & \exp -i\alpha(a+c_{j,j+1}) \end{pmatrix} T_\theta' \begin{pmatrix} \exp i\alpha(a+\epsilon_{j,j}) & 0 \\ 0 & \exp -i\alpha(a+c_{j,j}) \end{pmatrix} T_\phi' \qquad (20)$$

where,

$$T_\theta' = (Rvr)_\theta \qquad \ldots (21)$$

$$T_\phi' = (Rvr)_\phi \qquad \ldots (22)$$

The matrices R, v, r have the same meaning as in 1 and $(Rvr)_\theta$ means that the product has been taken at a θ potential well Now following the same argument as used in deriving equation (40) of (I), we see that for the present case—the allowed energies are given by the condition.

$$\mathrm{tr}\left(\prod_{j=n}^{j=1} T_j\right) \leqslant 2 \qquad \ldots \quad (23)$$

Retaining only upto the first order terms, we get from (20).

$$T_j = (T' + K_{j,j+1}T' + T_\theta K_{j,j} T_\varphi) \qquad \ldots \quad (24)$$

where,

$$T_\theta = \begin{pmatrix} \exp i\alpha a & 0 \\ 0 & \exp(-i\alpha a) \end{pmatrix} T_\theta' \qquad \ldots \quad (25)$$

$$T_\varphi = \begin{pmatrix} \exp(i\alpha a) & 0 \\ 0 & \exp(-i\alpha a) \end{pmatrix} T_\varphi' \qquad \ldots \quad (26)$$

$$K_{j,j} = \begin{pmatrix} i\alpha\epsilon_{j,j} & 0 \\ 0 & -i\alpha\epsilon_{j,j} \end{pmatrix} \qquad \ldots \quad (27)$$

$$T' = T_\theta T_\varphi \qquad \ldots \quad (28)$$

Substituting (24) in (23) and retaining again only upto the first order terms, we get :

$$\mathrm{tr}[T'^n + \sum_{j=1}^{j=n-1} (T'^{n-j} K_{j,j+1} T'^j) + \sum_{i=1}^{j=n} (T'^{n-j} T_\theta K_{j,j} T_\varphi T'^{j-1})] \leqslant 2 \qquad \ldots \quad (29)$$

Equating the zero and first order terms separately to zero, we get from (29) :

$$\mathrm{tr}\, T'^n \leqslant 2 \qquad \ldots \quad (30)$$

$$\mathrm{tr}\,[\sum_{j=1}^{j=n} (T'^{n-j} K_{j,j+1} T'^j + T'^{n-j} T_\theta \cdot K_{j,j} \cdot T_\varphi \cdot T'^{j-1})] = 0 \qquad \ldots \quad (31)$$

Now if $\cos c' = \frac{1}{2}\,\mathrm{tr}\, T'$, the eigen values of T' are $\exp(\pm ic')$ · [$\because \det T' = 1$]. The elements of T'^n are thus given by the same formulae as (9) and (10) with c_θ replace by c' and l by n With proper expressions for the elements of T'^n, we get from (30) :

$$\frac{1}{\sin c'} [\sin(n+1)c' - \sin nc' T'_{11r}] \leqslant 1 \qquad \ldots \quad (32)$$

where, $\qquad T'_{11} = (T_\theta T_\varphi)_{11} = T'_{11r} + iT'_{11I}$

Also using the proper expressions for the elements of T'^n and retaining again only upto the first order terms, we get from (31) :

$$\sum_{j=1}^{j=n-1} [\epsilon_{j,j+1}\{(T'^{n-j})_{11r}(T'^j)_{11I} + (T'^{n-j})_{11I}(T'^j)_{11r}\} +$$

$$+ \epsilon_{j,j}\{P_1 + P_2 + P_3 + P_4 - P_5 - P_6 - P_7 - P_8\}] = 0 \qquad \ldots \quad (33)$$

In equation (33), P_1, P_2 etc. are rather complicated expressions containing the real and imaginary parts of the elements of the matrices (T'^{n-j}), (T'^{j-1}), T_θ and T_φ. They can be worked out by straightforward multiplication of the matrices in the second term of the bracket [ ] in equation (31). To indicate the general nature of these terms, we write in full only P_1 :

$$\begin{aligned} P_1 \equiv & [(T'^{n-j})_{11r}(T_\theta)_{11r} - (T'^{n-j})_{11I}(T_\theta)_{11I}] \cdot \\ & [(T_\theta)_{11I}(T'^{j-1})_{11r} + (T'^{j-1})_{11I}(T_\theta)_{11r}] \\ & + [(T_\varphi)_{11r}(T'^{j-1})_{11r} - (T_\varphi)_{11I}(T'^{j-1})_{11I}] \cdot \\ & [(T'^{j-1})_{11I}(T_\theta)_{11r} + (T'^{n-j})_{11r}(T_\theta)_{11I}] \end{aligned} \quad \ldots (34)$$

The connections between $(T'^{n-j})_{12r}$, $(T'^{n-j})_{12I}$, $(T_\theta)_{12r}$, $(T_\theta)_{11I}$ etc which are the real and imaginary parts of $(T'^{n-j})_{12}$, $(T_\theta)_{11}$ etc are expressed by the following equations :

$$(T'^{n})_{11r} = (T'^{n})^*_{22} = (T'^{n})_{11r} + i(T'^{n})_{11I} \quad \ldots (35)$$

$$(T'^{n})_{12} = (T'^{n})^*_{21} = (T'^{n})_{12r} + i(T'^{n})_{12I} \quad \ldots (36)$$

$$(T_\theta)_{11} = (T_\theta)^*_{22} = (T_\theta)_{11r} + i(T_\theta)_{11I} \quad \ldots (37)$$

$$(T_\theta)_{12} = (T_\theta)^*_{21} = (T_\theta)_{12r} + i(T_\theta)_{12I} \quad \ldots (38)$$

$$(T_\varphi)_{11} = (T_\varphi)^*_{22} = (T_\varphi)_{11r} + i(T_\varphi)_{11I} \quad \ldots (39)$$

$$(T_\varphi)_{12} = (T_\varphi)^*_{21} = (T_\varphi)_{12r} + i(T_\varphi)_{12I} \quad \ldots (40)$$

The full expressions for $(T_\theta)_{11}$, $(T_\theta)_{11}$ ...etc are given by equations (5) to (8) with $\beta, v = \beta_1, v_1$ and $\beta, v = \beta_2, v_2$ for θ and ϕ type of atoms respectively and $a_1 = a_2 = a$.

Case 2 : Disordered molecular solid . we consider now the model of the solid as given by Fig. (5) below :

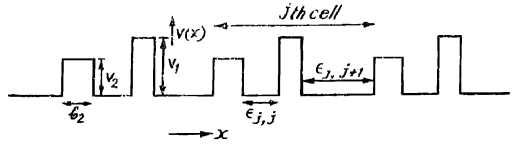

Fig 5

Rectangular potential-well model for a one-dimensional finite disordered molecular solid.

This model corresponds to a disordered one-dimensional molecular solid like NaCl where the potential at each molecular site is given by a pair of two different rectangular potential-wells. Thus we see that for the present model, $\epsilon_{j,j} = 0$ for all

j's. The allowed energies in the present case are given by equation (32) together with another equation given below :

$$\sum_{j=1}^{j=n} [e_{j,j+1}\{(T'^{n-j})_{11,r}(T'^{j})_{11I} + (T'^{n-j})_{11I} \cdot (T'^{j})_{11r}\}] = 0 \qquad \ldots \quad (41)$$

Equation (41) follows from (41) with $e_{i,j} = 0$. With the full expression for $(T'^{n-j})_{11r}$ etc., equation (41) can be further simplified to the following form .

$$\sum_{j=1}^{j=n} e_{j,j+1}[T'_{11I} \cos(n-2j-1)c' - 2T'_{11r}T'_{11I} \cdot$$

$$\cos(n-2j)c' \;] \cdot T'_{11I} \cos(n-2j+1)c' - 2T'_{11I} \cdot$$

$$\sum_{j=1}^{j=n} e_{j,j+1}\Big) [\cos(n+1)c' - T'_{11r} \cos nc') = 0 \qquad \ldots \quad (42)$$

DISCUSSIONS

In the work of this paper, we have used the matrix method of paper I to study the electronic energy-states of mixed crystals within the frame work of the rectangular potential-well model. We have derived the equations for allowed energies of several types of mixed lattices—both perfect and disordered. The allowed energies for the disordered models of Fig. (4) and (5) are given by two equations. One of these [Eqn. (32)] just gives the band structure of a perfect diatomic lattice, with a finite no of atoms (n) of both types. The other [Eqn. (42) for Fig. (5) and Eqn. (33) for Fig. (4)] gives additional energy-values due to disorder of the system. The additional energy-states due to disorder of the system affect the electrical conductivity to a great extent. With the help of a Green's function method the author (Roy 1964) has studied the models corrsponding to Fig. (4) and (5) in the framework of δ-function potentials. As has been discussed in I, the δ-function model suffers from several limitations compared to the rectangular potential-well model. Moreover to get the equations for allowed energies for the models of Fig. (4) and (5) using the matrix method, as is done in this paper, we have not used any particular equation connecting the wave functions at any two lattice points. Such an equation has been used in getting equations for allowed energies with the Green's function method. Thus the results obtained by the matrix method are expected to be more general than the results of Green's function method. It would be worthwhile to make numerical computations about the allowed electronic energies for various models, using the equations given by matrix method and Green's function method and compare these computations at least qualitatively with the experimental observations. An investigation in this line is under author's contemplation and the results will appear in later publications.

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